

ACTIVE METAL BRAZING OF CARBON-CARBON COMPOSITES TO TITANIUM

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ABSTRACT

The Ti-metal/C-C composite joints were formed by reactive brazing with three commercial brazes, namely, Cu-ABA, TiCuNi, and TiCuSi. The joint microstructures were examined using optical microscopy, and scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS). The results of the microstructure analysis indicate solute redistribution across the joint which led to good wetting, spreading, and metallurgical bond formation via interdiffusion.

1. INTRODUCTION

Carbon-carbon (C-C) composites are extensively used for the nose cone and leading edges of the space shuttle, as solid propellant rocket nozzles and exit cones, and as ablative nose tips and heat shield for ballistic missiles. The material also finds use in aircraft braking system where the extremely high frictional torque generates intense heat, raising the disk temperature to 500 °C, and the interface temperature to 2000 °C. Likewise, first wall tiles of fusion reactors also utilize C-C to cope with intense thermal loads. For the space exploration systems, metal/C-C composites have been proposed for applications in radiator and heat management applications, and in spacecraft, including turbine and turbopump housing, thrust cell jackets, and flanges. Most such applications will require joining C-C to metals. Robust assembly and integration technologies will, therefore, play an essential role in the development and manufacturing of parts using novel and conventional carbon-base materials [1-3]. Carbon-carbon has been brazed using Ag, Au and Cu-base filler metals for moderate use temperatures, and Zr and Hf metals, and HfB₂ and MoSi₂ powders for very high use temperatures [4-6].

In this paper, three commercial active metal brazes (Cu-ABA, TiCuNi, and TiCuSi) were used to create C-C/Ti joints. The microstructure and composition of the brazed joint were examined by optical and scanning electron microscopy (SEM) coupled with EDS. The effect of braze composition and processing conditions on the interfacial microstructure and composition of the joint regions is discussed in light of the wetting and spreading behavior of reactive brazes.

2. EXPERIMENTAL PROCEDURE

The carbon-carbon composites used in this study were obtained from C-CAT Composites, TX. These composites were made from T-300 C fibers and resin-derived carbon matrix. The composite panels were sliced into 2.54 cm x 1.25 cm x 0.25 cm pieces. Commercially pure Ti plates (Ti metal 75A) from TIMET, Inc., MO, were also cut into slices of the same size, and joined (on their broad faces) to C-C using intervening braze foils. The following commercial brazes obtained from Morgan Advanced Ceramics, Inc., were used for joining C-C composites to Ti: Cu-ABA, TiCuNi, and TiCuSi. The composition, and physical and mechanical characteristics of these brazes are summarized in Table 1. The braze foil thickness was ~50 µm.

All the materials were ultrasonically cleaned in acetone for 10 min. prior to use. The braze foil, cut to the size of Ti and C-C plates, was sandwiched between them, and a normal load of 0.30 N was applied to the assembly to hold them together. The assembly was heated to the brazing temperature under vacuum, isothermally held for 5 min., and then cooled to room temperature. The brazed samples were cut, mounted in epoxy, polished, and examined using optical and scanning electron microscopy (SEM) coupled with energy dispersive x-ray spectroscopy (EDS).

Table 1. Physical and Mechanical Properties of Cu-ABA, TiCuNi, and TiCuSi Brazes

Braze	Composition, wt%	T _L , K	T _S , K	CTE, 10 ⁻⁶ /K	Thermal Cond., W/m.K	Y.S., MPa	% Elong.
Cu-ABA	92.8Cu, 3Si, 2Al, 2.2Ti	1300	1231	19.5	38	279	42
TiCuNi	70Ti, 15Cu, 15Ni	1233	1183	20.3	--	--	--
TiCuSi	68.8Ag, 26.7Cu, 4.5Ti	1173	1053	18.5	219	292	28

T_L and T_S denote the liquidus and solidus temperatures of the braze, respectively.

3. RESULTS AND DISCUSSION

3.1 *Interface Microstructure*

Figures 1 through 9 display the interface microstructure of the joints made using the three braze materials. Both low- and high-magnification views of the C-C/braze interface for each of the braze materials indicate an intimate contact between the carbon and the braze. The interfaces are free of commonly-found structural defects such as microvoids and porosity. An interfacial interphase appears to have preferentially precipitated on the carbon surface in all the cases (Fig. 2, 4 & 6). The EDS analysis across the interface regions shows evidence of solute redistribution during brazing. High Ti concentrations were detected at the interface in C-C/TiCuNi (Fig. 4) and C-C/TiCuSi (Fig. 9) joints, suggesting possible formation of a Ti-rich interphase, such as TiC_{1-x}, which bonds well to both the carbon and the braze. At the braze/Ti interface (Figs. 5 & 8), some dissolution of the metal in the molten braze appears to have occurred, leading to near-interfacial changes in the composition. Overall, the interfaces appear to be microstructurally sound, and well-bonded due to interdiffusion of solutes and the formation of secondary phases.

The formation of TiC in Ti-containing brazes in contact with carbon is thermodynamically favorable. The Gibb's free energy change for TiC formation from the reaction $\text{Ti} + \text{C} \rightarrow \text{TiC}$ at the brazing temperature of 850 °C is -171.18 kJ, which indicates that TiC formation is highly likely. Thermodynamic calculations [7,8] also show that sub-stoichiometric carbides such as TiC_{0.95}, TiC_{0.91}, TiC_{0.80}, TiC_{0.70}, TiC_{0.60} and TiC_{0.48} could form from Cu alloys in which the activity of Ti is greater than 0.1. As the solubility of Ti in Cu at the brazing temperature of 850 °C is high, its activity coefficient may be large enough to cause the formation of these carbides. With reference to the Cu-ABA braze, it should be noted that it contains Si in addition to Ti, and both silicon carbide and titanium carbide could form from the reaction of Si and Ti with carbon. The Gibb's free energy change for SiC formation ($\text{Si} + \text{C} \rightarrow \text{SiC}$) at 850 C is -62.76 kJ which suggests that SiC formation during brazing is thermodynamically possible.

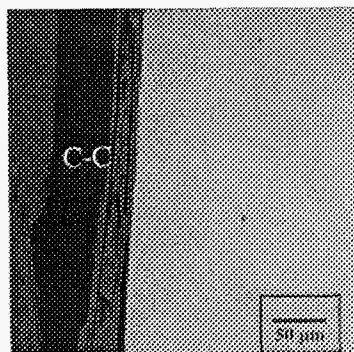


Fig. 1 C-C/Cu-ABA interface region.

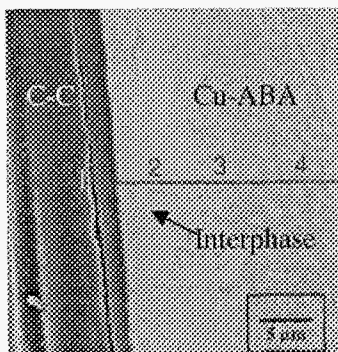


Fig. 2 C-C/Cu-ABA interface: 1) 100C; 2) 34Cu, 56Ti, 8Si, 2Al; 3) 24Cu, 60Ti, 7Si, 8Al; and 4) 91Ti, 4Si, 5Al.

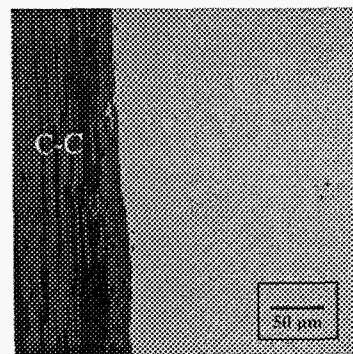


Fig. 3 C-C/TiCuNi interface.

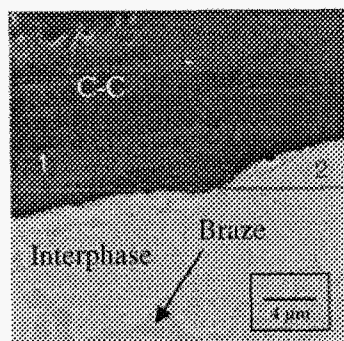


Fig. 4 C-C/TiCuNi interface: 1) 100%C; and 2) 54% Cu, 38%Ti, 7%Ni.

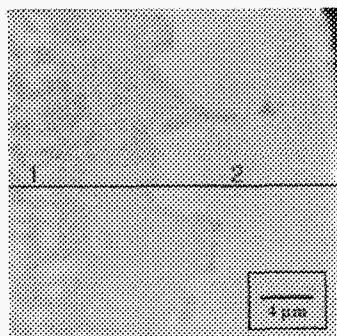


Fig. 5 TiCuNi/Ti interface: 1) 47Ti, 8.5Ni, 45Cu and 2) 52Ti, 23Ni, 25Cu.

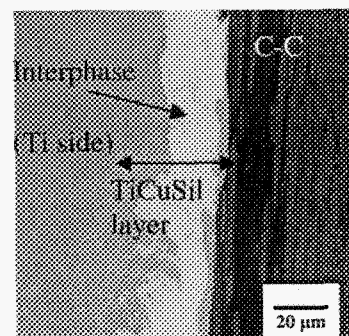


Fig. 6 C-C/TiCuSil interface showing secondary phase precipitation.

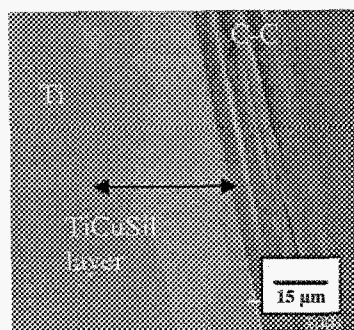


Fig. 7 Interface between TiCuSil and C-C.

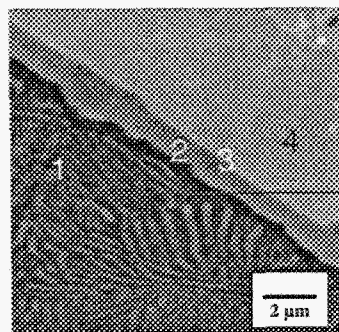


Fig. 8 Ti/TiCuSil interface: 1) 85Ti, 15Ag; 2) 75Ti, 25Ag; 3) 41Ti, 35Cu, 24Ag; and 4) 38Ti, 44Cu, 18Ag.

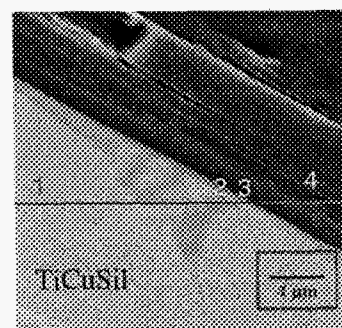


Fig. 9 C-C/TiCuSil interface: 1) 100Ag; 2) 55Cu, 39Ag, 6Ti; 3) 67Ti, 33Ag; and 4) 100 C.

3.2 *Braze Spreading*

The interface microstructures presented in Figs. 1-9 show that the Ti-metal/braze/C-C joints are free of interfacial microdefects, and exhibit excellent physical contact and good metallurgical bonding. The literature data compiled in Table 2 and Fig. 10 show that Ti additions to Ag, Cu, CuSn, and NiPd alloys sharply decrease the contact angle, θ , and promote braze spreading on carbon. Usually, short brazing times suffice for maximum spread; for example, θ approaches 0° in 5 min. for Cu-12%Ti melt in contact with vitreous C [15]. Pure Cu and Ag do not wet graphite ($\theta \sim 137^\circ$ - 140°), but the addition of Ti [7,9,12] and/or Si [16] improves the wetting through the formation of carbides (TiC and SiC) at the interface. One of our brazes, Copper-ABA, contained Si besides Ti, and Si is known to react with and lower the contact angle on carbon ($\theta \sim 0^\circ$ for Si/C [13,14]). In the case of Ti as a reactive solute in braze, both TiC and various substoichiometric titanium carbides with different C/Ti ratios could form. These carbides are readily wetted by Cu [7].

The interface microstructures of our joints displayed in the photomicrographs of Figs. 1 through 9 do not show evidence of braze penetration in the C-C substrate even though the brazes wet and spread on the C-C substrate. With porous graphite, Naidich and coworkers [9,12] and Sobczak et al [11] noted that Cu-Ti alloys both wetted and impregnated the graphite (this was in contrast to the behavior exhibited by the Cr-containing Cu brazes in which the reaction layer was dense and sealed the open porosity in the carbon, thus blocking melt penetration [11]). With Ti in braze, the TiC reaction layer was discontinuous with a non-homogenous structure [11] that permitted penetration of porous carbon by the melt.

Table 2. Contact Angles of Various Ti-Containing Alloys on Carbon

Alloy [ref.]	Temp., K	Contact Angle, deg.
Ag-0.1wt%Ti [9]	1273	$45^1, 85^2$
Ag-0.45wt%Ti [9]	1273	5^1
Ag-1.0wt%Ti [9]	1273	7^2
NiPd-50wt%Ti [10]	1523	16^3
Ni-45wt%Pd [10]	1523	137^3
Cu-9.2wt%Ti [15]	1350	0^3
Cu-17.5wt%Ti [11]	1373	10^4
CuSn-50at%Ti [12]	1473	11^3

¹diamond, ²graphite, ³vitreous C, ⁴porous graphite.

The absence of capillary pressure-driven braze infiltration in our systems could be due to the higher density and relatively low open porosity of our C-C substrate materials in comparison to those used in ref. [11]. Besides Ti carbides, other interfacial compounds could also form at the interface in Ti-containing brazes; for example, formation of a wettability-enhancing, metal-like interfacial layer of TiO at the carbon/metal interface has been reported in the literature. The formation of this layer in our joints is not unlikely especially because stable oxides of Ti form even at oxygen partial pressures as low as $\sim 10^{-28}$ atm., which most likely existed in the brazing atmosphere.

Thus, even though the base metals copper and silver are inert to carbon and oxygen, reactive Ti possesses high affinity toward both oxygen and carbon, which could form titanium oxides and titanium carbides. Likewise, the nickel in TiCuNi also has a higher affinity for carbon than Cu, Au and Ag, and has been found to segregate at the carbon/ metal interface (e.g., in Au/C). Even though there are no stable carbides in the Ni-C system, many workers have reported

the formation of a metastable Ni_3C carbide due to interaction of liquid Ni with solid C; this leads to the reasonably good wettability with relatively low contact angles ($68\text{--}90^\circ$ [14]) of Ni on carbon. However, as the principal constituent of TiCuNi is Ti ($\sim 70\%$) which strongly reacts with the carbon, formation of nickel carbide in our joints is less probable.

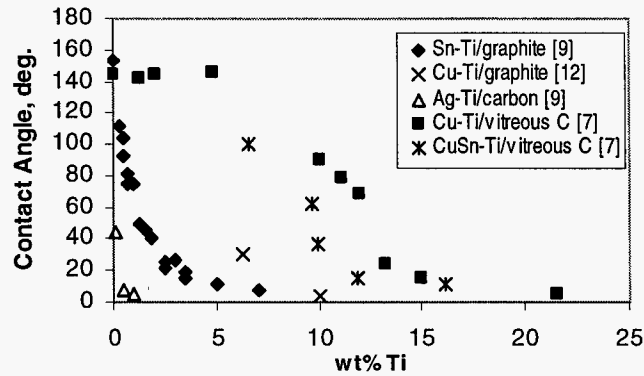


Fig. 10. Effect of Ti in Cu, Sn and Ag alloys on contact angle with C.

3.3 Thermal Considerations

The thermal response of the C-C/Ti joints is important for high heat flux applications (e.g., spacecraft radiators, heat exchangers). Cu, Ag and Ti were the principal constituents of our brazes, with the Ag and Cu brazes (Cu-ABA and TiCuSil) containing Ti as an active metal. While Ti alloying usually decreases the thermal conductivity, the relatively small Ti content of our Ag and Cu brazes will not be very detrimental to the braze conductivity. On a positive note, Ti additions to Cu decrease the melting point of Cu, which makes braze spreading easier, leading to the formation of a good joint.

The thermal conductivity of TiCuSil is 219 W/m.K (Table 1) which compares favorably with that of 3D C-C composites (quoted as $60\text{--}190 \text{ W/m.K}$ [17]), although with a Cu-ABA joint (conductivity $\sim 38 \text{ W/m.K}$), higher thermal resistance to heat dissipation may occur. A large thermal discontinuity will be encountered at the braze/Ti interface as well because the conductivity of commercially pure Ti is only 16.0 W/m.K . It will be necessary to perform thermal management tests on joint assemblies in the geometric configuration that they will be used in an actual radiator or heat exchanger to understand how these interfaces will modulate the heat flow.

A comparison of the room-temperature values of CTE of Cu-ABA and TiCuSil (Table 1) with the CTE of C-C (quoted as $0\text{--}1.0 \times 10^{-6}/\text{K}$ over $20\text{--}250^\circ\text{C}$, and $2.0\text{--}4.0 \times 10^{-6}/\text{K}$ over $20\text{--}2500^\circ\text{C}$ for the 3D composites [17]) shows that the CTE mismatch ($\Delta\alpha$) is very large, and will likely result in large thermal stresses due to differential expansion (contraction) at the C-C/braze interface during brazing and service. However, the relatively large ductility (Table 1) of brazes will likely accommodate the thermal stresses, thus preventing interfacial cracking and joint failure. This agrees with the absence of interfacial cracking and disjoining in Figs. 1-9. A simple calculation shows that the thermal strain, $\Delta\alpha\Delta T$, for a brazing temperature range of 850°C to room temperature (25°C), will be 1.36×10^{-2} , 1.28×10^{-2} , and 1.43×10^{-2} , respectively, for the Cu-ABA, TiCuSil, and TiCuNi joints. These thermal strains exceed the yield strain (on the order of 10^{-3}) of our braze alloys, which suggests that plastic yielding at the interface may not be unlikely even if it is noted that some of the alloying elements in the braze material will provide solid-solution hardening. The interface between the Ti metal and the braze has a smaller CTE

mismatch (CTE of commercial purity Ti is $8.6 \times 10^{-6}/\text{K}$) than the CTE mismatch at the C-C/braze interface. As a result, less severe thermal stress concentration is anticipated at this interface. Mechanical strength characterization of the joints is currently underway to understand the effects of braze type and brazing process variables on the interfacial bonding, and will be reported in a separate publication.

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References

1. D. Lewis III and M. Singh, "Post-processing and assembly of ceramic-matrix composites"; pp. 668-673 in *ASM Handbook*, **21**, ASM Int., Mater. Park, OH, 2001.
2. D. Goodman and R. Singler, "Joining carbon-carbon composites and high-temperature materials with high energy electron beams", *NASA CR 97*, 206679 (1998).
3. M.G. Nicholas, 'Active metal brazing'; pp. 73-93, *Joining of Ceram.*, Chapman & Hall, 1990.
4. "Joining of C-C and ceramic-matrix composites", NSWC Presentation from the Interagency Planning Group, Becker, ed., *IDA Memo Report M-312*, T.F. Kearns, ed. (April 1987).
5. "Joining of C-C and ceramic-matrix composites", Mater. Innovations Lab Presentation, Interagency Planning Group, Yalof, ed., *IDA Memo Report M-312*, T.F. Kearns (April 1987).
6. P. Dadras, "Joining of carbon-carbon composites by using MoSi_2 and Ti interlayers", Proc. of the 14th Conf. Metal-, Carbon- and Ceramic-Matrix Compos., *NASA CP 3097*, Part 2: J.D. Buckley, ed. (1990).
7. R. Standing and M. Nicholas, 'The wetting of alumina and vitreous carbon by Cu-Sn-Ti alloys', *J. Mater. Sci.*, **13** 1509-1514 (1978).
8. E.K. Storms, '*Refractory Carbides*', Academic Press, New York, 1967.
9. Y.V. Naidich, 'The wettability of solids by molten metals', pp. 353-484 in *Progress in Surf. and Membrane Sci.*, Cadenhead and Danielli (eds.), **14**, Acad. Press, NY, 1981.
10. N. Grigorenko, V. Poluyanskaya, N. Eustathopoulos, and Y. V. Naidich, 'Wettability and spreading of Ni and Ni-Pd melts over SiC and vitreous C'; pp. 27-35 in *Proc. 2nd Int. Conf. on High-Temp. Capillarity*, Eustathopoulos and Sobczak (eds.), Foundry Res. Inst. (Krakow), 1997.
11. N. Sobczak, J. Sobczak, M. Ksiazek, W. Radziwill and J. Morgiel, 'Interaction between Ti or Cr containing Cu alloys and porous graphite', pp. 97-98 in *Proc. 2nd Int. Conf. on High-Temp. Capillarity*, Eustathopoulos and Sobczak (eds.), Foundry Res. Inst. (Krakow), 1997.
12. N. Grigorenko, V. Poluyanskaya, N. Eustathopoulos, and Y. Naidich, 'Kinetics of spreading of some metal melts over covalent ceramic surfaces'; pp. 69-78 in *Interfacial Sci. of Ceram. Joining*, Bellosi et al (eds.), Kluwer Acad. Publ., Boston, 1998.
13. J. T. Whalen and A.T. Anderson, *J. Amer. Ceram. Soc.*, **34**[4] 378-383 (1976).
14. M. Humenik, Jr. and W.D. Kingery, 'Metal-ceramic interactions: III. Surface tension and wettability of metal-ceramic systems', *J. Amer. Ceram. Soc.*, **37**[1] 18-23 (1954).
15. J.G. Li, 'Wetting of Cu-Ti on Al_2O_3 and C', *J. Mater. Sci. Lett.*, **11** 1551-1554 (1992).
16. O. Dezellus, F. Hodaj and N. Eustathopoulos, 'Mechanisms of spreading in reactive Cu-Si/C system'; pp. 75-84 in *Trans. JWRI*, Osaka Univ., Eustathopoulos et al (eds.), 2001, JWRI.
17. R. Taylor, "Carbon-matrix composites"; in *Comprehensive Composite Materials*, **4** pp. 387-426, Elsevier Science Ltd., Boston, 2000.